

Hydrogen permeation properties of Pd-coated Pd₃₃Ni₅₂Si₁₅ amorphous alloy membrane

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The vast majority of experimental techniques used for the measurements of hydrogen permeability through metallic membranes whose one or both surfaces are covered with a thin Pd film is based on the assumption that a ratio of film-to-membrane thickness is small enough to cause hydrogen flow to be independent of the Pd film thickness. In an attempt to verify this assumption, we have measured the hydrogen flow through the Pd₃₃Ni₅₂Si₁₅ amorphous membrane covered with Pd film of 10, 20, and 30 nm in thickness. Contrary to our expectations, we have found a dramatic decrease in hydrogen flow with the increase in Pd film thickness. Our findings are discussed in terms of potential barrier between the two different phases.

Keywords: *permeability; hydrogen; palladium alloys; membrane; metallic glasses*

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1. Introduction

Palladium membranes as well as palladium-based alloys are highly permeable and selective for hydrogen diffusion. This makes them attractive materials for application in membranes reactors, fuel cells, and hydrogen-containing mixture sensors [1, 2]. For decades, pure palladium has been known for its high permeability for hydrogen. However, its high cost as well as structural deformation caused by hydride formation limits its industrial application. Therefore, current research trends concentrate on searching for alloys as well as on modification of their surface and structure to get a hydrogen permeability effect similar to that of pure palladium.

In many experimental techniques, including electrolytic methods, hydrogen permeability through the membranes whose one or two surfaces are coated with a thin Pd film [3] is measured. It

is usually assumed that the presence of Pd layer does not affect hydrogen flow. In an attempt to verify this assumption, we have measured hydrogen permeability through an amorphous Pd₃₃Ni₅₂Si₁₅ membrane coated with Pd film with a thickness of 10, 20 and 30 nm.

2. Experimental

An amorphous tape of Pd₃₃Ni₅₂Si₁₅ alloy with a width of 25 mm and 50 μm in thickness was prepared by a roller spinning method. The amorphicity of the alloy was confirmed by using X-ray micro-analyzer (WDS) as well as by X-ray diffractometry (Cu K, 40 kV, 30 mA). Electron microscopy (SEM) method was employed in order to verify the chemical composition of the alloy. Thermal stability of an amorphous phase was examined by differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s. No changes in sample structure were noticed at temperatures below 718 K. A disc with a diameter of 24 mm was cut from the tape and put

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into an analysis chamber. A schematic diagram of the analysis chamber along with the pumping station is depicted in Fig. 1.

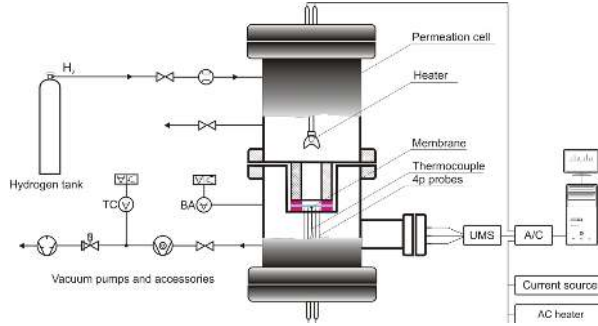


Fig. 1. Apparatus for measuring hydrogen permeation.

Hydrogen diffusion flow through the amorphous membrane coated with palladium was measured using a residual gas analyzer (measurements of partial pressure), employing the method described elsewhere [4, 5]. The changes in hydrogen flow were measured in a temperature range of 294 to 358 K, and at pressure fixed at 102 kPa. The initial pressure in the analysis chamber was 1×10^{-6} Pa.

Palladium layers of 10, 20 and 30 nm thickness were evaporated onto one of the membrane surfaces by using an electron beam technique. The thickness of the evaporated layer was measured using a quartz crystal microbalance.

3. Results and discussion

Fig. 2 shows the changes in hydrogen flow through a clean amorphous membrane as well as that coated with a palladium film as a function of temperature.

If hydrogen permeation is controlled by the diffusion process in the membrane, hydrogen flux, J [$\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$], is proportional to the difference of the square roots of hydrogen partial pressures between both sides, p_{out} and p_{in} [Pa] [6]:

$$J = DK \frac{\sqrt{p_{\text{out}}} - \sqrt{p_{\text{in}}}}{d} \quad (1)$$

where d [m] and $DK = P$ [$\text{mol}/(\text{ms}\cdot\text{Pa}^{1/2})$] are the thickness and the permeability, respectively.

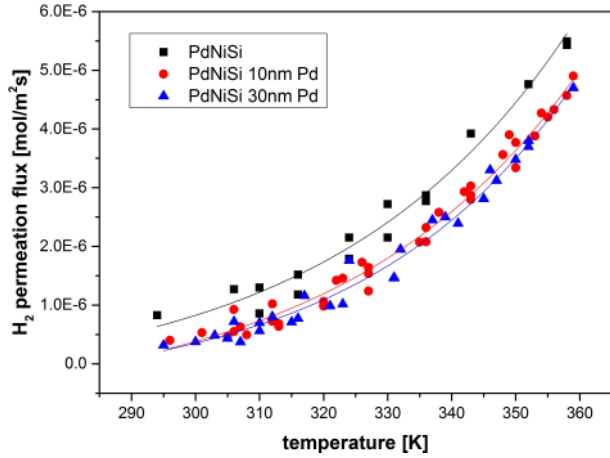


Fig. 2. Hydrogen flux as a function of temperature.

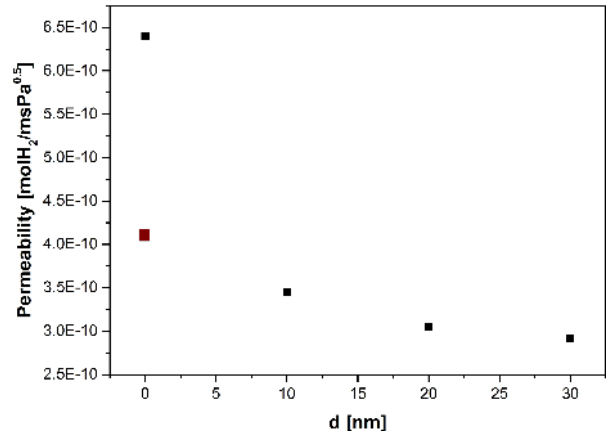


Fig. 3. Hydrogen permeability as a function of palladium layer thickness at temperature 300 K.

As in our experiment $p_{\text{out}} \gg p_{\text{in}}$ we can write equation 1 in a simplified version:

$$J = P \frac{\sqrt{p_{\text{out}}}}{d} \quad (2)$$

According to the theory [7, 8], the total hydrogen permeability through a membrane composed of several layers may be given by the following formula:

$$P = \frac{d_{\text{PdNiSi}} + d_{\text{Pd}}}{\frac{d_{\text{PdNiSi}}}{P_{\text{PdNiSi}}} + \frac{d_{\text{Pd}}}{P_{\text{Pd}}}} \quad (3)$$

where Pd and PdNiSi refer to palladium layer and amorphous membrane, respectively. Since in our

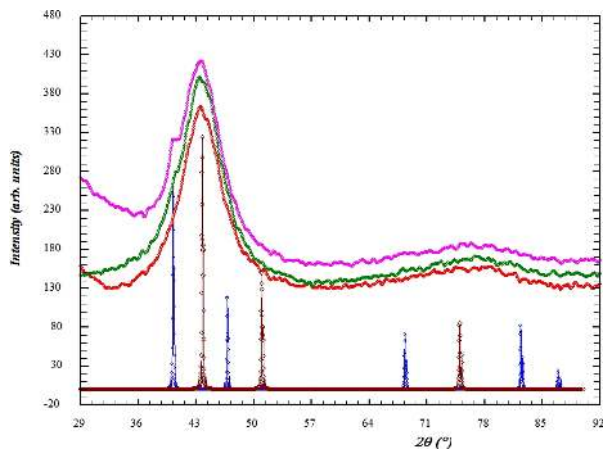


Fig. 4. X-ray diffraction patterns for Pd-coated $\text{Pd}_{33}\text{Ni}_{52}\text{Si}_{15}$ amorphous alloy. Theoretical diffractograms of PdNiSi (brown) and Pd (blue) crystals are presented at the bottom.

experiment the thickness of palladium layer was by far lower than the thickness of the membrane ($d_{\text{Pd}} \ll d_{\text{PdNiSi}}$), then, according to the theory, the permeability of the Pd-coated membrane should be the same as the permeability of the amorphous membrane. What is more, hydrogen flow through the membrane should be not influenced by the Pd layer. However, as shown in Fig. 3 the obtained results do not support this theory.

The brown point refers to the value of hydrogen flow, derived from the theory (it is noteworthy that this value is by far lower than those of the hydrogen flow through a clean membrane). Therefore, it is clear that introducing Pd layer onto the amorphous membrane results in the decrease in hydrogen flow, which is by far lower than the one that can be inferred from literature. Similar results have been described in [8]. Introducing Pd layer onto both surfaces of a membrane made of $\text{Ni}_{20}\text{Nb}_{20}\text{Ta}_5\text{Zr}_{30}\text{Co}_5$ resulted in the increase in hydrogen flow, while a decrease in hydrogen flow was noticed after introducing Pd layer onto an external or internal membrane surface. These effects have been accounted for in terms of the changes in catalytic properties of membrane surface caused by Pd atoms diffusion inward into the membrane surface. The explanation of the observed decrease in hydrogen flow in terms of Pd atom diffusion is not satisfactory. In our opinion, the driving force of the observed

effect, is the ordering of the layer in addition to the chemical composition of both the membrane and deposited layer. A roentgenogram (Fig. 4) has been taken from the deposited layer in order to examine its structure.

It is clearly seen that a thin Pd polycrystalline film forms on the surface of the amorphous membrane. We propose that the transition from the amorphous structure into the polycrystalline one is the mechanism behind the changes in hydrogen permeability through a Pd-covered membrane.

4. Conclusions

We have examined the influence of palladium thin film deposited onto one side of an amorphous $\text{Pd}_{33}\text{Ni}_{52}\text{Si}_{15}$ alloy membrane on the hydrogen permeation flux at pressure fixed at 102 kPa and at temperature range of 294 to 358 K. On the basis of obtained results we conclude that, the deposited Pd layer results in the decrease in the hydrogen flow through the membrane. This decrease is by far larger than that, which can be expected from the theory. We have found that this effect is due to amorphous-to-polycrystalline transition of the membrane structure. The surface of the amorphous membrane provides hydrogen atoms with a larger number of active centers as compared to the partially ordered Pd layer. This leads to an increase in hydrogen concentration on the inner membrane layer.

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